



Polyoxometalate-based Ionic liquid as thermoregulated and environmentally friendly catalyst for starch oxidation

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ABSTRACT

A new kind of polyoxometalate (POM) ionic liquid ($[(\text{CH}_3)_3\text{NCH}_2\text{CH}_2\text{OH}]_5\text{PV}_2\text{Mo}_{10}\text{O}_{40}$) (abbreviated as $\text{Ch}_5\text{PMo}_{10}\text{V}_2\text{O}_{40}$) has been synthesized by a precipitation/ion exchange method with choline chloride and $\text{H}_5\text{PMo}_{10}\text{V}_2\text{O}_{40}$ as precursors. The produced salt turned out to be an original ionic liquid (IL) catalyst and exhibited a novel switchable property based on temperature variation. In this regard, it refers to a thermoregulated feature that elevated temperature leads to the miscibility of catalyst and substrate. As decreasing the temperature, the catalyst precipitates and becomes heterogeneous form to be separated automatically from the reaction mixture. The combination of POMs with choline chloride was also proved to be effective in catalyzing the oxidation of starch, which showed higher or nearly identical performance with traditional catalysts, such as FeSO_4 . Results demonstrated the catalyst was easily separated from the products and the retrieved $\text{Ch}_5\text{PMo}_{10}\text{V}_2\text{O}_{40}$ could be repeatedly used without appreciable loss of its performance, which highlighted the practical application of this important biomass.

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1. Introduction

Growing concerns about global warming and the limitation of fossil fuels are pushing scientists to spare their efforts on the production of chemicals and fuels from biomass in a more efficient and sustainable way [1]. Among the different options, starch is one kind of abundant feedstocks for the production of hydrophilic starch, which is generally obtained from the partial oxidation of native starch, and is widely used in paper and textile industries. The hydrophilic starch, as sugar acid, is primarily achieved by controlling oxidation of starch through biocatalysis or chemical catalysis [2]. Several oxidative processes can be accounted including the use of alkaline hydrogen peroxide [3], nitrogen oxidizes [4], sodium hypochlorite [5], peracetic acid [6], oxone [6] and sodium periodate [7]. The above processes showed efficient, but brought about environmental problems that large amount of waste was seriously discharged, and sometimes over oxidation resulting in low yields. Thus, more attractive processes are urged to be developed by using H_2O_2 or O_2 as environmentally acceptable oxidants. By now, easily acceptable and inexpensive transition-metal

catalysts have been used [8–10] in H_2O_2 or O_2 system. Fe or Cu salts have been reported to catalyze starch oxidation in yields up to 90–99%, but lower carbonyl and carboxyl contents (0.04 molCO per 100 g, $\text{DS}_{\text{C=O}} = 0.066$, $0.009 \text{ molCO}_2\text{H}$ per 100 g, $\text{DS}_{\text{CO}_2\text{H}} = 0.014$. DS means the degree of substitution) [8] were obtained. Inorganic salt, Na_2WO_4 , exhibited a relatively high catalytic activity in oxidizing of starch with H_2O_2 , yielding exclusively oligomeric polyhydroxycarboxylic acids with a high acid concentration ($0.11 - 0.25 \text{ molCO}_2\text{H}$ per 100 g) [10]. Iron phthalocyanine (FePcS) gave the oxidative compounds with carbonyl and carboxylic groups as 0.05 molCO per 100 g, $\text{DS}_{\text{C=O}} = 0.08$, $0.024 \text{ molCO}_2\text{H}$ per 100 g, $\text{DS}_{\text{molCO}_2\text{H}} = 0.04$, respectively [11]. Fenton-type reagents FeSO_4 and CuSO_4 showed efficient to transform starch into polyhydroxycarboxylic acids with the highest yields, $0.61 \text{ molCO}_2\text{H}$ per 100 g [12], which was the best result reported to date. However, the solubility of catalyst in products would give rise to the difficulty on separation, and the system stability may be further interfered by the impurities. Another relatively higher degree of oxidation was acquired by the three-component system $\text{CH}_3\text{ReO}_3/\text{H}_2\text{O}_2/\text{HBr}$ in water–acetic acid mixture for the selective oxidation of the C6 hydroxymethyl group yielding the corresponding carboxylic acid with 0.52 molCO per 100 g [13]. Even though, the above system required large amount of CH_3ReO_3 to ensure the activity due to the deactivation. Therefore, an essential element of the as-described catalytic oxidation of starch is the use of environmentally benign oxidants, H_2O_2 or O_2 , in combination with ideal catalyst.

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Recently, polyoxometalates (POMs) have drawn much attention due to their diverse availability in electronic, magnetic, redox, medicine and photonic fields, etc. Among numerous applications of POMs, catalysis is by far the most attractive one for its high flexibility in modification of the redox properties, ease of handling, environmental compatibility, non-toxicity and experimental simplicity [14]. One of catalytically important subclass of Keggin compounds are the mixed vanadium (V)-substituted polyoxometalates. Mizuno and Kamata had reviewed the recent developments on the catalytic oxidation of hydrocarbons with hydrogen peroxide by vanadium-based polyoxometalates [15]. The proposed reaction based on vanadium substituted POMs includes hydroxyl and hydroperoxy radicals generated by homolytic cleavage of H_2O_2 and vanadium center, whose mechanism is similar to that of Fenton type reactions. Thus, vanadium substituted POMs with Keggin structure, $\text{PV}_2\text{Mo}_{10}\text{O}_{40}^{5-}$, was chosen in the present work to catalyze the oxidation of starch to produce carbonyl and carboxyl groups.

The application of ionic liquids as environmentally benign reaction solvents for synthesis and catalysis has received extensive attention [16] during these years. Moreover, POM-based ILs have also attracted substantial investigations in chemistry field in recent years [17–20]. Accordingly, we have interacted choline chloride (ChCl ; $\text{HOCH}_2\text{CH}_2\text{N}(\text{Me})_3\text{Cl}$), which is one of the most economically and readily available ionic liquids, with $\text{H}_5\text{PMo}_{10}\text{V}_2$ as alternative to realize the oxidation of starch. Owing to its less expensive than most other ionic liquids, low toxic to humans, environmentally friendly and non-flammable characters [21], choline chloride has been used in the conversion of carbohydrates into 5-hydroxymethylfurfural [21–23]. The combination of ChCl with Lewis acids, such as ZnCl_2 , has also been investigated in *o*-acetylation of cellulose and monosaccharides [24].

To the best of our knowledge, there is no report on the combination of ChCl with POMs to act as oxidative catalysts in the conversion of starch into carboxylic acids. The aim of this work is to seek a simple approach to prepare POM catalysts which could be used as heterogeneous catalysts to catalyze starch oxidized to its corresponding oxidation product with high efficiency under mild reaction conditions.

2. Experimental

2.1. Materials

All chemicals were purchased from commercial sources and were used as received without further purification. 0.1 M of NaOH solution was used for determining the carboxyl content by titration. $\text{H}_5\text{PV}_2\text{Mo}_{10}\text{O}_{40}$ was synthesized according to Ref. [25], and identified by IR spectroscopy.

2.2. Physical measurements

Elemental analysis was carried out using a Leeman Plasma Spec (I) ICP-ES and a P-E 2400 CHN elemental analyzer. IR spectra ($4000\text{--}400\text{ cm}^{-1}$) were recorded in KBr discs on a NicoletMagna 560 IR spectrometer. The ^{31}P NMR (85% H_3PO_4 external standard) measurements were obtained using a Bruker AM500 spectrometer at 202.5 MHz. X-ray diffraction (XRD) patterns of the catalyst were collected on Rigaku Dmax 2000 X-ray diffractometer with $\text{Cu K}\alpha$ radiation ($\lambda = 0.154178\text{ nm}$) (Rigaku Corporation). TEM image was determined by JEM-2100F instrument. Energy dispersive X-ray analysis (EDX) was performed to take into account of the C, N, P, V and Mo elements.

2.3. Catalyst preparation

$\text{Ch}_5\text{PMo}_{10}\text{V}_2\text{O}_{40}$ was synthesized by mixing aqueous solution of ChCl and $\text{H}_5\text{PV}_2\text{Mo}_{10}\text{O}_{40}$ with a molar ratio of 5:1. Once $\text{H}_5\text{PV}_2\text{Mo}_{10}\text{O}_{40}$ solution added dropwise into the solution of ChCl , an orange precipitate was observed immediately. Then removed the solid by filtration and washed with diluted water until no free of POMs and chloride (AgNO_3 test) found. Finally dried in air under ambient conditions. IR (1% KBr pellet, $4000\text{--}400\text{ cm}^{-1}$): 1050, 943, 874, and 787 cm^{-1} . Anal. Calcd for $\text{Ch}_5\text{PMo}_{10}\text{V}_2\text{O}_{40}$: C, 13; N, 3.1; P, 1.3; V, 4.5 and Mo, 42.5%. Found: C, 11; N, 3.7; P, 2.3; V, 4.3 and Mo, 43.1%.

2.4. Starch oxidation

In a typical reaction protocol, 1 g of starch and 4 mg of catalyst was mixed with 1.5 mL distilled water in the reactor, and heated to required temperature with continually and vigorously stirred for a period. Then the oxidation reaction was activated by addition certain amount of hydrogen peroxide. In order to make the starch oxidized completely as much as possible, the hydrogen peroxide was added intermittently other than the whole amount at once. Furthermore, the H_2O_2 addition interval depends on the length of experiment, usually at a rate of $900\text{ }\mu\text{L}/2\text{ h}$ when 10 h reaction time and 4.5 mL hydrogen peroxide was required. After reaction, the soluble product was filtrated immediately and dried at room temperature to get white paste resulting material, which weight was almost up to 0.95 g.

The recycle reaction was carried out using 10 g of starch and 40 mg of catalyst. After reaction, the soluble product was filtrated and the remaining mixture contained water, unreacted H_2O_2 and catalysts. Then the catalyst was separated by centrifuge at 4000 rpm, washed with water for reused. The leaching amount of the catalyst was determined by ICP-ES.

2.5. Determination of carboxyl content [12]

300 mg of resulting material (white paste) was dissolved in distilled water (20 mL), and a few drops of phenolphthalein solution in EtOH were added as indicator. The solution was titrated with 0.1 M of NaOH solution until the color of the solution changed to pink.

3. Results and discussion

3.1. Characterization of $[(\text{CH}_3)_3\text{NCH}_2\text{CH}_2\text{OH}]_5\text{PV}_2\text{Mo}_{10}\text{O}_{40}$

From the results of the elemental analyses, the C, H, N, Mo, P and V contents in catalyst are C, 2.76; H, 0.71; N, 0.70; P, 1.45; Mo, 40.92; V, 4.22%, respectively. Compared with the calculated values C, 2.66; H, 0.62; N, 0.62; P, 1.37; Mo, 42.60; V, 4.52%, the results are satisfactory.

The FT-IR spectra are quite useful to identify structural and bonding changes in the Keggin unit present in POM-based IL hybrid materials. Fig. 1a gave the four characteristic peaks of IR spectrum of $\text{Ch}_5\text{PMo}_{10}\text{V}_2\text{O}_{40}$ at 1055, 951, 867, 791 cm^{-1} , respectively. Compared to its parent $[\text{PV}_2\text{Mo}_{10}\text{O}_{40}]^{5-}$ with four characteristic peaks of P–O stretching ($\sim 1064\text{ cm}^{-1}$), M–O_{ter} stretching ($\sim 964\text{ cm}^{-1}$), Mo–O_c–Mo stretching of inter bridges between corner-sharing MoO_6 octahedra ($\sim 876\text{ cm}^{-1}$), and Mo–O_e–Mo stretching of intra bridges between edge-sharing MoO_6 octahedra ($\sim 814\text{ cm}^{-1}$), four characteristic peaks of Keggin structure are intact. In addition, the peaks at 3394, 3028 and 1473 cm^{-1} were attributed to C–H, and C–N, respectively, showing that quaternary ammonium existed in $\text{Ch}_5\text{PMo}_{10}\text{V}_2\text{O}_{40}$.

As can be seen from ^{31}P MAS NMR spectra of $\text{H}_5\text{PV}_2\text{Mo}_{10}\text{O}_{40}$ and $\text{Ch}_5\text{PMo}_{10}\text{V}_2\text{O}_{40}$ (Fig. 2), the peak at 4.75 ppm for $\text{Ch}_5\text{PMo}_{10}\text{V}_2\text{O}_{40}$,

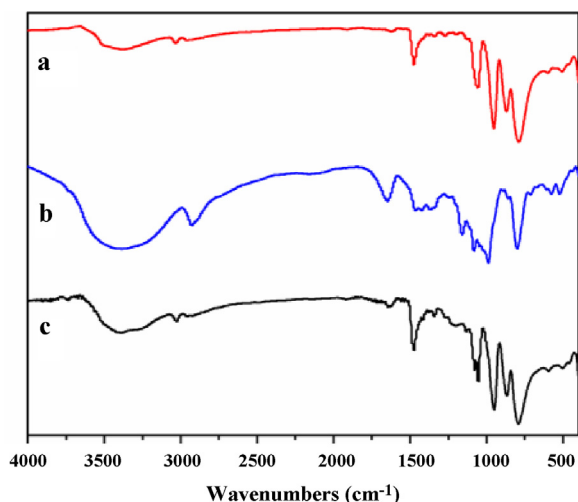


Fig. 1. The IR spectra of pure $[(CH_3)_3NCH_2CH_2OH]_5PV_2Mo_{10}O_{40}$ (a), $[(CH_3)_3NCH_2CH_2OH]_5PV_2Mo_{10}O_{40}$ after absorbing starch (b) and $[(CH_3)_3NCH_2CH_2OH]_5PV_2Mo_{10}O_{40}$ after the oxidation of starch (c).

corresponding to $H_5PV_2Mo_{10}O_{40}$ signal at 4.55 ppm, displayed a little shift of 0.20 ppm, indicating that $PV_2Mo_{10}O_{40}^{5-}$ remains intact upon assembly, and the little shift can be attributed to the different chemical environment of choline chloride. Next, the XRD pattern of $CH_5PMo_{10}V_2O_{40}$ (Fig. S1) gave three diffraction peaks at 2.87, 7.29, and 23.50°, which can be regarded as the feature of the POM.

To further identify dispersing morphology of the composite catalyst in water, transmission electron microscopy (TEM) was investigated with a combination of elemental analysis by energy-dispersive X-ray (EDX) spectroscopy. The TEM image (Fig. 3 left) shows that the $CH_5PMo_{10}V_2O_{40}$ catalyst consists of irregular particles with overall sizes ranging from 10 to 20 nm. Elemental analysis carried out using EDX (Fig. 3 right) revealed the presence of several elements including Mo (41.74%), P (1.37%), V (4.56%), N (0.68%), respectively, which confirmed the formula of the POM-based IL as $CH_5PMo_{10}V_2O_{40}$.

3.2. Oxidative activity of $[(CH_3)_3NCH_2CH_2OH]_5PV_2Mo_{10}O_{40}$ catalyst

The oxidative products had been characterized by FT-IR spectroscopy (Fig. 4), which obtained from oxidation of starch using 0.4 wt.% of $CH_5PMo_{10}V_2O_{40}$ in the presence of H_2O_2 . The presence

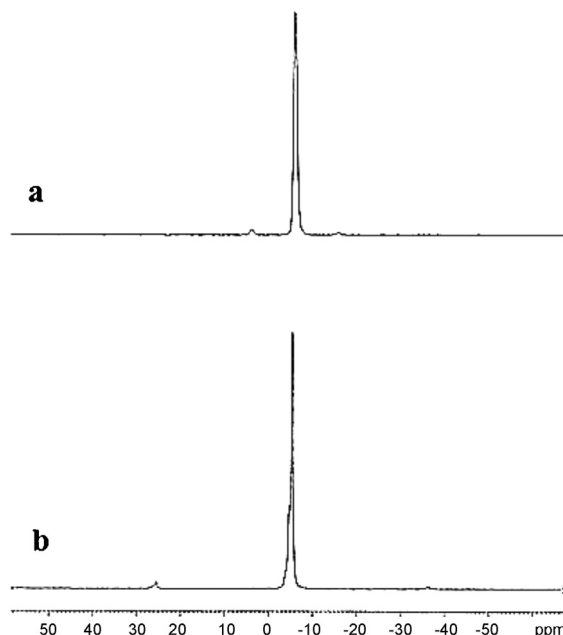


Fig. 2. The ^{31}P MAS NMR spectra of $H_5PV_2Mo_{10}O_{40}$ (a) and $[(CH_3)_3NCH_2CH_2OH]_5PV_2Mo_{10}O_{40}$ (b).

of an intense ν_{CO} band at 1740 cm^{-1} can be attributed to carboxylic groups, indicating that $CH_5PMo_{10}V_2O_{40}$ indeed exhibited a catalytic behavior toward starch oxidation by H_2O_2 .

Bras's group [12] had reported the oxidation of starch with $FeSO_4 \cdot 7H_2O$ (0.1 wt.%) and H_2O_2 (100 wt.%), which gave a large amount of soluble product with the highest acid content (0.61 mol_{CO_2H} per 100 g) at 60°C for 24 h. However, complexation and discoloration of the starch had been found. In order to evaluate the performance of $CH_5PMo_{10}V_2O_{40}$, the contrast test has been done under our reaction conditions. As comparison, other catalysts including $FeSO_4$, $ChCl$, and $H_5PV_2Mo_{10}O_{40}$ have been used (Table 1). The catalytic activity was in the range of $ChCl < H_5PV_2Mo_{10}O_{40} < FeSO_4 \sim CH_5PMo_{10}V_2O_{40}$. It can be seen that $H_5PV_2Mo_{10}O_{40}$ exhibited a relatively high catalytic activity (0.50 mol_{CO_2H} per 100 g) in oxidation of starch by H_2O_2 , which was attributed to its highest oxidative property and solubility in water. $ChCl$, however, only acts as a solvent in this oxidation reaction, and revealed a low performance over the oxidation of starch. Obviously, the catalytic activity of $CH_5PMo_{10}V_2O_{40}$ was fairly comparable to

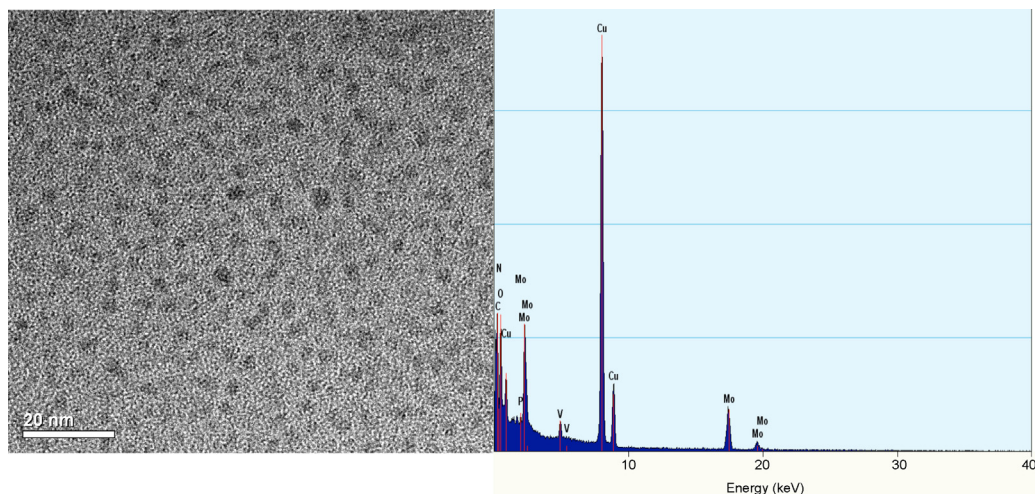


Fig. 3. The TEM image of $[(CH_3)_3NCH_2CH_2OH]_5PV_2Mo_{10}O_{40}$ (left) and EDX pattern (right).

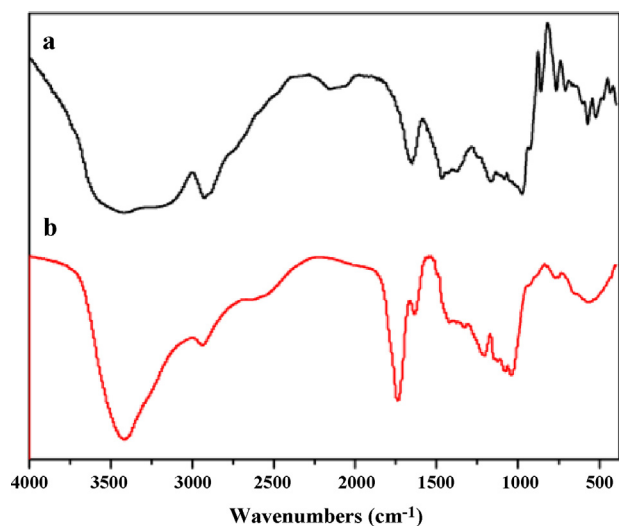


Fig. 4. IR spectra of native starch (a) and oxidized starch in the presence of 0.4 wt.% $[(CH_3)_3NCH_2CH_2OH]_5PV_2Mo_{10}O_{40}$ and 30 wt.% H_2O_2 (b).

that of $FeSO_4$. More importantly, $Ch_5PMo_{10}V_2O_{40}$ was still in its solid form after reaction, which held quite benefits in separation. This result is considerably important since there are only a few successful examples at present, and the catalytic activity and stability of this heterogeneous vanadium substituted POMs are comparable to those of the homogeneous analogs [15].

Compared to $H_5PV_2Mo_{10}O_{40}$, the higher activity of $Ch_5PMo_{10}V_2O_{40}$ derived from both the oxidative center of $PV_2Mo_{10}O_{40}^{5-}$ and the thermoregulated property of POM-IL. It can be seen that the catalyst $Ch_5PMo_{10}V_2O_{40}$ dispersed around the reactor with heterogeneous form both before reaction (Fig. 5a) and after reaction when the temperature was dropped to room temperature (Fig. 5c). As increasing the temperature up to 70 °C, $Ch_5PMo_{10}V_2O_{40}$ changed into homogeneous form and uniformly dispersed around the reactor (Fig. 5b). The morphology of the catalyst in this phase was tested by TEM (Fig. 3), showing that $Ch_5PMo_{10}V_2O_{40}$ assembled as micellar spheres with sizes around nanometers. The absorption of starch by these micelles has been detected through IR spectrum of the after absorbed $Ch_5PMo_{10}V_2O_{40}$, which was processed with stirring $Ch_5PMo_{10}V_2O_{40}$ and starch together for certain time. Seen from the IR spectrum (Fig. 1b), the peak at 2927 cm^{-1} could be attribute to the original starch, suggesting that certain amount of starch was gathered closely to this catalyst. Meanwhile, the peaks corresponding to POM anion shifted, indicating that some interaction occurs between the O atom from glucose monomer and the terminal oxygen atom from the POM molecules. As for the peak of the original glucose monomer at 1167 cm^{-1} , C–O–C stretching shifts to 1163 cm^{-1} due to the interaction between C–O–C and POMs. These results fairly confirmed that the

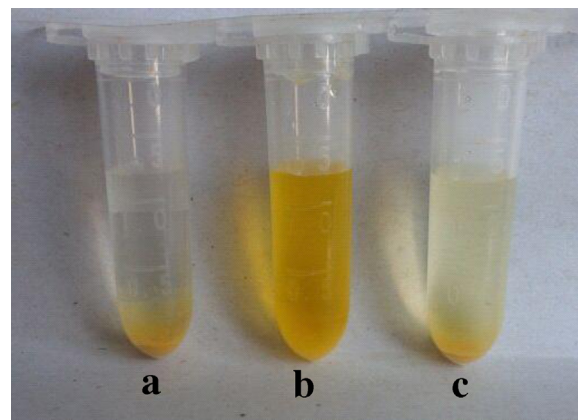


Fig. 5. The states of $[(CH_3)_3NCH_2CH_2OH]_5PV_2Mo_{10}O_{40}$ (a) before the reaction at room temperature (b) during the reaction at 70 °C (c) after the reaction at room temperature.

interaction between the catalyst and starch occurred, which further proved that $[(CH_3)_3NCH_2CH_2OH]^+$ group possesses the absorption ability for starch. That is to say, starch was accumulated through interactions with the catalyst surface or through insertion into the nanoreactor itself. Hereby, three synergistic effects generated the superior results: the thermoregulated property of POM-IL; the aggregation of starch molecules around nano-POM catalyst; and the inherent oxidative activity of $H_5PV_2Mo_{10}O_{40}$.

Main parameters affecting the oxidation reaction including temperature, reaction time, catalyst dosage and H_2O_2 concentration were investigated as following (Fig. 6). The oxidation of starch by H_2O_2 was supposed to depend on temperature. Fig. 6a gives the carboxyl content of oxidized starch as a function of temperature, while reaction was carried out using 4.5 mL H_2O_2 as oxidant in the presence of 4 mg $Ch_5PMo_{10}V_2O_{40}$ as catalyst for 10 h. It can be seen that the carboxyl content increased with increasing the temperature up to 70 °C. Further raising the temperature did not result in higher carboxyl contents. As a predominant factor, reaction time significantly affected the oxidation of starch by H_2O_2 . Fig. 6b showed the effect of reaction time on the degree of starch oxidation expressed as carboxyl content under the same reaction conditions. It showed that the carboxyl content increased with the reaction time up to 10 h. Keeping increasing the reaction time to 12 h, no further increase in the carboxyl content of oxidized starch can be obtained. Fig. 6c showed the effect of H_2O_2 concentration on the carboxyl content when the reaction was carried out at 70 °C for 10 h with 4 mg of catalyst. Obviously, the carboxyl content increased markedly by increasing H_2O_2 concentration up to 4.5 mL. However, further increasing the H_2O_2 concentration did not give higher carboxyl content, which could be ascribed to the decomposition of H_2O_2 to O_2 and H_2O . As a result, the optimum H_2O_2 concentration was found to be 4.5 mL.

3.3. The regeneration of the catalyst

As mentioned above, this thermoregulated catalyst $Ch_5PMo_{10}V_2O_{40}$ can be readily recovered by decreasing the temperature with slightly loss (Fig. 5c). Also, its catalytic activity on starch oxidation remained high-efficiency after six times repeated experiments (Fig. 6d). Moreover, the total amount of $Ch_5PMo_{10}V_2O_{40}$ leaching over six runs of reaction was only 6.8% that of the initial amount. The IR spectrum of the catalyst after the reaction also indicated its stability during the oxidative reaction (Fig. 1c). Therefore, the leaching test revealed that $Ch_5PMo_{10}V_2O_{40}$ has excellent stability and could be reused about six times as a rapid heterogeneous catalyst by a simple treatment.

Table 1
Oxidation of starch by H_2O_2 with different catalysts.^a

Entry	Catalyst	Amount (wt.%)	CO_2H (mol per 100 g)
1	–	–	0.23
2	ChCl	0.4	0.28
3	$FeSO_4 \cdot 7H_2O$	0.4	0.54
4	$H_5PV_2Mo_{10}O_{40}$	0.4	0.50
5	$[(CH_3)_3NCH_2CH_2OH]_5PV_2Mo_{10}O_{40}$	0.3	0.53
6	$[(CH_3)_3NCH_2CH_2OH]_5PV_2Mo_{10}O_{40}$	0.4	0.59
7	$[(CH_3)_3NCH_2CH_2OH]_5PV_2Mo_{10}O_{40}$	0.5	0.54
8	$[(CH_3)_3NCH_2CH_2OH]_5PV_2Mo_{10}O_{40}$	0.6	0.48

^a Reaction conditions: starch (1 g), H_2O_2 (4.5 mL, 30%), H_2O (1.5 mL), 70 °C, 10 h.

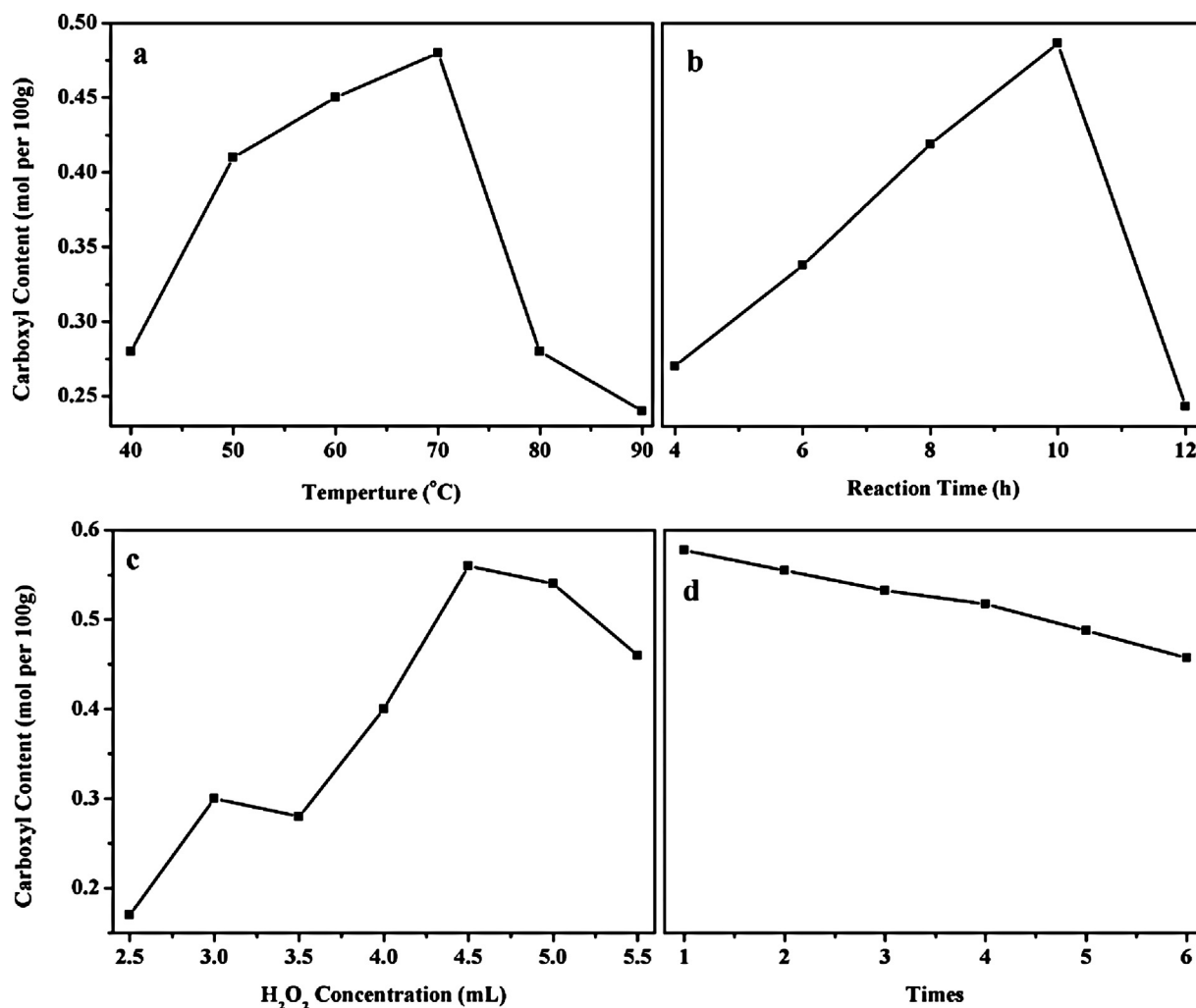


Fig. 6. Parameters affecting the oxidation reaction including temperature (a), reaction time (b), H₂O₂ concentration (c), and reuse (d).

3.4. The possible mechanism

Generally, oxidation of organic molecules by POMs is recognized as a free radical mechanism [26]. Hydroxyl radical (OH•), an extremely high-potential oxidizing agent with a short life, can oxidize organic substrates and generate other free radicals [27]. To determine the main active species responsible for the oxidation of starch catalyzed by $\text{CH}_5\text{PMo}_{10}\text{V}_2\text{O}_{40}$, a comparative study was undertaken for the scavenger-loaded conditions (Fig. 7). The formation of possible oxidative intermediate species, such as singlet oxygen ($^1\text{O}_2$), superoxide ($\text{O}_2^{\bullet-}$), and hydroperoxy (HO_2^{\bullet}), or (OH•), under otherwise identical conditions was investigated indirectly with the use of appropriate quenchers for these species. Certain quenchers including KI (a quencher of OH• radical on catalyst surface [28]), sodium azide (NaN_3 , a singlet oxygen quencher [29] but may also interact with OH• radical [30]), and *p*-benzoquinone ($\text{C}_6\text{H}_4\text{O}_2$, BQ, a quencher of superoxide radical [31]). The adding of NaN_3 and KI affect the oxidation of starch throughout the experiment, indicating that the active oxidative species involved in this system was either $^1\text{O}_2$ or OH•. The effect of NaN_3 was higher than that of KI, showing that, besides OH•, single oxygen $^1\text{O}_2$ was formed as a possible oxidative intermediate species during the reaction. BQ does not affect the oxidation of starch, showing that $\text{O}_2^{\bullet-}$ was not the oxidative intermediate species. These results demonstrated that the reaction took place through a radical and single oxygen mechanism.

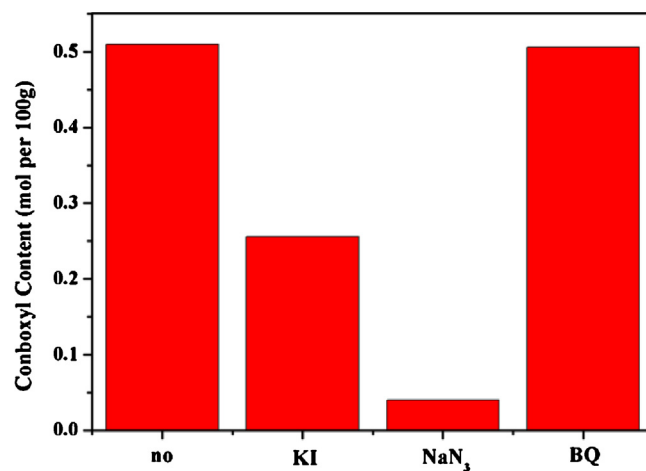


Fig. 7. Effects of scavenging agents on oxidation of starch in the presence of 2 mM of 1,4-benzoquinone (BQ), NaN_3 and KI with 4 mg of $\text{CH}_5\text{PMo}_{10}\text{V}_2\text{O}_{40}$, 4.5 mL of H₂O₂, 1.5 mL of water, at 70 °C for 10 h.

4. Conclusion

The $\text{CH}_5\text{PMo}_{10}\text{V}_2\text{O}_{40}$ catalyst has been synthesized using choline chloride and $\text{H}_5\text{PMo}_{10}\text{V}_2\text{O}_{40}$ as building blocks, which resulted in nonconventional POMs-IL in solid state at room temperature. It

was used as a “temperature controlled self-separation catalyst” for oxidation of starch due to its property of switching from homogeneous to heterogeneous system, which made the recovery and reusability quite convenient. Also this POM-IL catalyst exhibited higher efficiency in catalytic oxidation of starch with H_2O_2 with a degree of oxidation of 0.59 $\text{mol}_{\text{CO}_2\text{H}}$ per 100 g under the mild conditions, which was comparable to traditional homogeneous catalyst FeSO_4 . It is supposed to be a promising approach for converting renewable feedstocks (carbohydrates, vegetable oils, terpenes and lignocellulosic materials) into valuable chemicals and polymers. Its competitive advantages can be summarized as (1) Easily synthesis of $[(\text{CH}_3)_3\text{NCH}_2\text{CH}_2\text{OH}]_5\text{PV}_2\text{Mo}_{10}\text{O}_{40}$; (2) Thermoregulated catalysis, which means it could be used as a homogeneous catalyst for oxidation of starch when raising the temperature. Moreover, decreasing of the temperature could make the catalysts precipitate and it is pretty easily recycled without any regeneration approaches used, just like a heterogeneous system. That is, this POM-IL catalyst hold the advantages of both homogeneous and heterogeneous catalysis; (3) Highly efficiency (0.59 $\text{mol}_{\text{CO}_2\text{H}}$ per 100 g) on producing of polyhydroxycarboxylic acids; (4) The absence of complexation products with oxidized starch (in contrast to the traditional FeSO_4 , which forms complexation and discoloration products of the starch).

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.apcatb.2013.02.028>.

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